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LIGNIN CONVERSION - AN OVERVIEW

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ABSTRACT

Lignins are complex amorphous polymers which contain 30%-40% of the heat content in woody feedstocks. Biomass pretreatment alters chemical composition and properties of the resulting lignins. The aromatic complex nature of lignins suggests that they can be converted into mixtures of low-molecular-weight compounds that could be excellent liquid fuels. Various approaches could be used in this conversion. For instance, a mild hydrodeoxygenation and dealkylation leads to a mixture of substituted phenolic compounds and aromatic hydrocarbons as main products. The phenolics can be converted into methyl aryl ethers (MAE). The mixture of MAE and aromatic hydrocarbons has a high value as a low-vapor pressure octane enhancer that is fully compatible with gasoline. Other routes of conversion are possible. Because of the complexity of lignins, it is our strategy to produce mixtures of acceptable products such that separation costs that have plagued lignin utilization for one product routes are minimized. An integral part of lignin conversion into liquid fuels is lignin characterization which helps identify feedstock characteristics that make them most suitable for biochemical conversion. The characterization studies identify key chemical structures present in the lignins after pretreatment which have to be modified to transform these low-molecular-weight polymers into liquid fuels. Extractives and other bark-derived materials are isolated with the lignins after chemical modification in the pretreatment step and will be processed with lignins.

LIGNIN CONVERSION - AN OVERVIEW

INTRODUCTION

Lignins are complex amorphous phenolic polymers which cannot be fermented to ethanol. Lignins are present in higher plants to provide a vascular system for mechanical reinforcement and conduction of solutes over extended distances (Adler 1977; Sarkanen and Ludwig, eds 1971; Fengel and Wegener 1984; Sjostrom 1981, Sarkanen 1975; Glasser in press). Lignins together with the cellulose and other cell wall polymers make a tissue of excellent strength and durability. The molecules of lignins are built quite differently from those of polysaccharides (empirical formula of anhydroglucose $CH_{1.7}O_{0.8}$), as they consist of an aromatic system composed of phenylpropane units (hardwood lignin empirical formula $CH_{1.2}O_{0.5}$). Lignification in plants is a result of the need to conduct water and to elevate the leaves, needles, and crown for improved solar energy conversion. In addition, lignins contribute to the storage of energy in the plants, the improvement of resistance to biodegradation, and the improvement of resistance towards changes in humidity and atmospheric degradation because lignins are very good antioxidizing agents. They contribute to the improvement of soil properties during natural plant decay. Herbaceous plants can be made to have very low lignin content. Lower lignin contents are associated with annual plants in which the need to provide long-term resistance towards biodegradation is not as high (Adler 1977; Sarkanen and Ludwig, eds 1971; Fengel and Wegener 1984; Sjöström 1981, Sarkanen 1975; Glasser in press).

Lignins are present in 18%-33% by weight in various wood species and in variable smaller amounts in herbaceous plants and agricultural residues (Goldstein 1981). Lignin is the biomass component of highest specific heat content (11,300 Btu/dry lb compared to cellulose at 7,400 Btu/dry lb), or about 30%-40% of the overall wood heat content. For herbaceous species, lignin represents 10%-20% of the overall heat content. Woody feedstocks are probably the most suited for lignin conversion, though if the process uses multiple feedstocks, lignin conversion will be important for both types of feedstocks (Adler 1977; Sarkanen and Ludwig, eds 1971; Fengel and Wegener 1984; Sjöström 1981, Sarkanen 1975; Glasser in press).

Lignin is a high-molecular-weight natural product formed initially by the enzymatic dehydrogenation of p-hydroxycinnamyl alcohols (Fig. 1), which yields resonance-stabilized phenoxy radicals (Fig. 2). The ultimate step in lignin formation is a free-radical coupling of monomeric units, not subject to enzymatic control. The types of bonds that can result between the radicals shown in Fig. 2 are exemplified in Fig. 3. The main type of bonding between monomeric units in lignins is an ether bond linking the side chain to the aromatic structures of the monomeric C_9 (phenylpropane) units. The main position is the β- (center of side chain) and the secondary is the α-O-4. The proportions of the various types of bonds for representative woods is shown in Table 1. Therefore, lignins differ from other natural products (polysaccharides, proteins, and nucleic acids) by having a random distribution of at least ten types of bonds. Two main types of lignins are: the guaiacyl lignins, in which alcohol precursors with one methoxy substitutent in the p-hydroxy cinnamyl alcohol molecule dominate (characteristic of softwoods), and the guaiacyl-syringyl lignins, in which
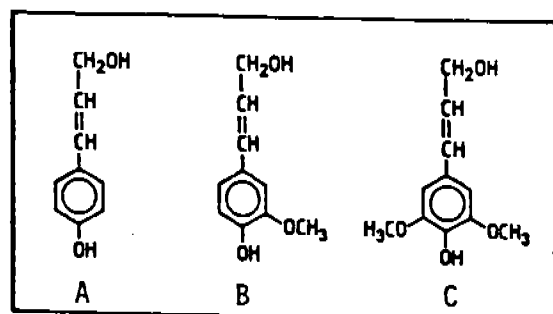
Figure 1.   The building units of lignins, the
cinnamyl alcohols: p-coumaryl alcohol (A),
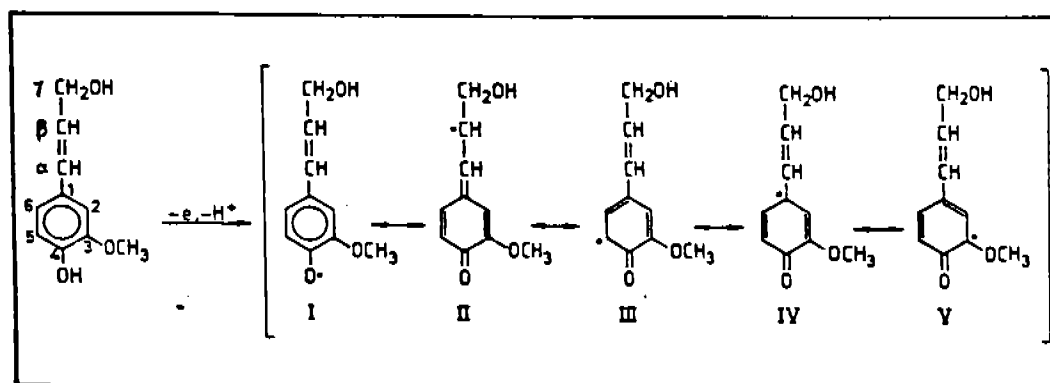coniferyl alcohol (B), and sinapyl alcohol (C)..

Figure 2. Enzymatic dehydrogenation of coniferyl alcohol yielding
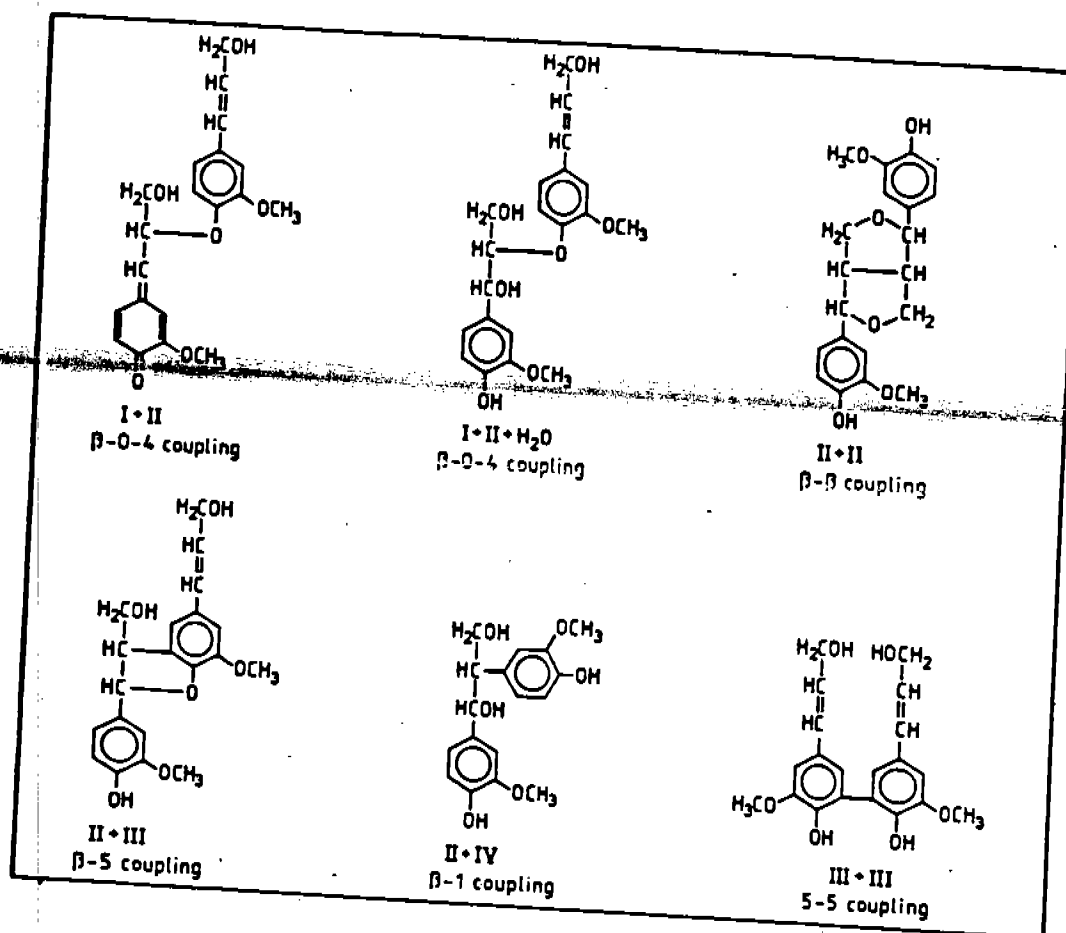   phenoxy radicals.

Figure 3. Typical dilignol structures. Roman numerals refer to Fig. 2.

I+II: Quinonemethide
I+II+H$_2$O: Guaiacylglycerol-β-coniferyl ether
II+II: D,L-Pinoresinol
II+III: Dehydroconiferyl alcohol
II+IV: 1,2-Diguaiacylpropane-1,3-diol
III+III: Dehydrobisconiferyl alcohol

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both monomethoxy- and dimethoxy-substituted p-hydroxy cinnamyl alcohols predominate. Hardwoods and grasses contain guaiacyl-syringyl lignins; grasses and hardwoods also contain acids esterified to the lignin macromolecular core such as p-hydroxybenzoic acid (in hardwoods, principally aspen and other Populus species) and p-coumaric and ferulic acids (grasses). Most of the comments in this overview will be directed towards wood species. The investigation of the structure of the lignins in the herbaceous species of interest to the program is a promising subject of future studies.

Table 1. Proportions of Main Different Types of Bonds Connecting Phenyl-Propane Units in Milled Wood Lignins From Various Species. See Fig. 3 for Examples of Structures (Adler 1977).

Type of Structure	Proportions, %
	Spruce (Picea abies) Guaiacyl
Arylglycerol-β-aryl ether (β-0-4)	48
Biphenyl (β-β)	9.5-11
Phenylcoumaran (β-5)	9-12
Noncyclic benzyl (α) aryl ethers	6-8
Pinoresinol (β-β)	2
Diphenyl ether	3.5-4
Condensed structures in 2- or 6-positions	2.5-3

Type of Structure	Birch (Betula verrucosa) Guaiacyl	Syringyl	Total
Arylglycerol-β-aryl ether (β-0-4)	22-28	34-39	60
Biphenyl (β-β)	4.5		4.5
Phenylcoumaran (β-5)			6
Noncyclic benzyl (α) aryl ethers			6-8
Syringaresinol (β-β)			3
Diphenyl ether	1	5.5	6.5
Condensed structures in 2- or 6-positions	1-1.5	0.5-1	1.5-2.5

Lignin Utilization

The use of lignins for process fuel is the main utilization route for the conventional kraft pulping industry. Of the 20 million tons of kraft lignins and 1.5 million tons of lignosulfonates (from sulfite pulping processes) produced roughly 35,000 tons of kraft lignins and 700,000 tons of lignosulfonates are consumed worldwide in a variety of industrial products (1980 data, Lin 1983). These products cover a wide range of applications such as animal feed binding, water treatment, oil well drilling, soil stabilization, concrete additives, dyestuff dispersant, asphalt emulsion, protein precipitation, gypsum board additives, metal refining aids, and

others (Lin 1983). The effectiveness of lignins in these applications is generally attributed to their dispersing, binding, complexing, and emulsion stabilizing properties. A central issue concerning lignin utilization is the lack of reliable structure/property/performance relationships. Lignins inherent heterogeneity and complexity may lead to products which are deficient for applications where petrochemicals have been used because of their homogeneity of chemical functionalities and tailored reproducible molecular weight distributions (Lin 1983). Only recently have inroads been made into a systematic understanding of structure/performance/property relationships for lignins in various polymeric applications such as urethanes and in other engineered plastics (Glasser 1987).

In 1985, with the collaboration of Professor Wolfgang Glasser and chemical market analyst Pat Rice, we analyzed the potential markets for lignin-derived products which could have a bearing on the economics of ethanol production (Chum et al. 1985). Projections in terms of potential intensities of demand were made for a variety of applications for the year 2000. These numbers are only measures of potential intensity of demand and not projections of actual shipments of lignins. The report demonstrated that if fuel ethanol production in the billions of gallons scale were built in the future (most likely beyond the year 2000) lignin markets overall would **not** be saturated. Polymeric utilization was reviewed; fertilizers and biocides markets were not reviewed in detail. Initial evaluation of the markets for low-molecular-weight fuels and chemicals began. Such markets were later investigated is some detail by Gaines and Karpuk (1987). The low-molecular-weight phenol and liquid fuels markets are very large (see Fig. 4).

The fact that lignins are aromatic compounds in polymeric form, chemically close to the aromatic high-octane component of gasoline, makes them uniquely suited for the conversion into mixtures of compounds to be used as liquid fuels. These mixtures have high octane values and are fully compatible with present transportation liquid fuels derived from petroleum. A typical empirical formula for a methyl aryl ether (MAE) fuel is $CH_{1.3}O_{0.11}$ and that for a typical high-octane xylene aromatic hydrocarbon is $CH_{1.25}$. Pretreated lignins from hardwoods-to-ethanol processes have lower oxygen content than the milled wood lignins and are closer to the MAE but still require deoxygenation.

Several methods can be employed to convert lignins into liquid fuels that are compatible with petroleum-derived fuels. Hydrotreatment and pyrolysis are two examples of methods that can be used. The end products of full hydrodeoxygenation can be hydrocarbon fuels or, in case of milder processing, mixtures of phenolic compounds and aromatic hydrocarbons. Mild hydrodeoxygenation can lead to high yields of phenolic compounds for the production of methyl aryl ethers (MAE) and aromatic hydrocarbons that are liquid fuels and octane enhancers. Milder processes consume less hydrogen and may be more cost-effective because the end-products have a higher value as octane enhancers.
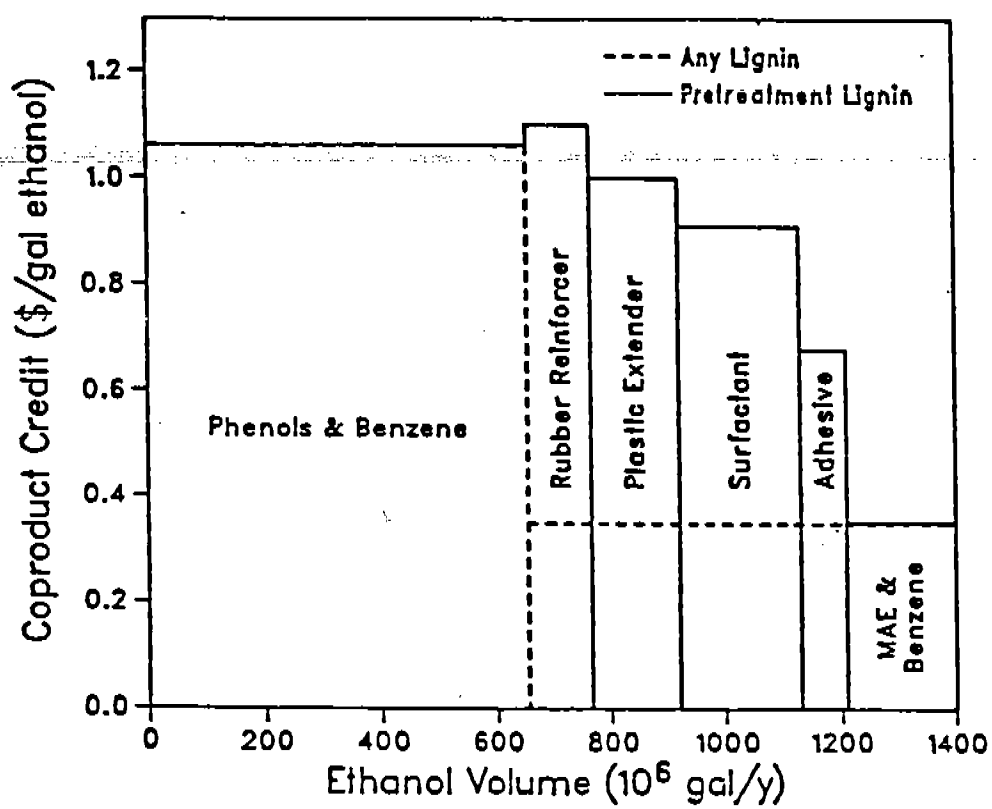
Figure 4. Lignin Coproduct Credits and Markets (Gaines and Karpuk 1987).

Lignin conversion to methyl aryl ethers (MAE) and hydrocarbons complements ethanol production. It allows full utilization of the feedstock. The cost-effectiveness of such routes needs to be investigated in more detail. Initial results indicate that credits of $0.35/gallon of ethanol would result leading to an overall more cost-effective production of liquid fuels from biomass. MAE have been already fleet tested and are accepted as octane enhancers that are fully compatible with gasoline (Singerman 1980). Another advantage of MAE and aromatic hydrocarbons is that they have lower vapor pressure than methanol and other volatile oxygenated octane enhancers. Therefore, their presence in gasoline allows refiners to add more of the volatile inexpensive butanes into the gasoline. In addition, if the refineries do not need to produce as much of the aromatic fraction for increased octane, the severity of cracking needed is minimized, and consequently energy utilization and total yields of gasoline from crude oil are improved (Van Tassel 1985).

Since lignin's reactivity is intrinsically very high because of its chemical make-up, built with a diversity of bonds and reactive groups that are easily oxidizable, and can undergo a variety of acid- and base-catalyzed hydrolysis reactions, attempts to remove lignins from the wood or other lignocellulosic composites induce substantial chemical changes. The understanding of these chemical reactions and the resulting polymers allow us to optimize subsequent conversion into liquid fuels. The knowledge is also applicable to other desired polymeric applications. The program addresses the isolation and analysis of lignins from the pretreatments that are most suited for enzyme hydrolysis of the resulting cellulosic residues. It investigates pretreated lignins chemical structure and the integration of the isolation with the subsequent upgrading to a liquid fuel. Looking at the overall processes, it is important to realize that not only the lignin fraction would be isolated and converted. In most of the pretreatments of interest, extractives would be isolated with the lignins and also need to be converted. When whole wood from the short-rotation woody species program is used, it is not likely that bark will be removed because of the cost of debarking and the use of relatively small diameter trees. Therefore, the characterization and further processing need to address the additional materials that will be generated in these pretreatments and be carried with the lignin fraction. Juvenile wood and a large amount of bark will be some of the operational materials the conversion will address.

Economic trade-offs between the various pretreatments and overall conversion processes will be carried out in order to select the most promising process options as well as careful investigation of the chemical and enzyme processes themselves. Lignin removal from the cellulosic residues is desirable for simultaneous saccharification and fermentation (SSF) process point of view. Digester volume is minimized, unreacted solids can be recycled without inert components accumulating in the SSF, and adsorption of enzyme components on the lignins is minimized (Wright et al. in press, Himmel et al. in press, Sutcliffe and Saddler 1987). It is desirable for high cost-effectiveness of the processes to recycle the enzymes in the process (Wright et al. in press). Thus, the overall program addresses wood species relevant to the ORNL feedstock production program and the full utilization of the feedstock in an integrated way.

Lignin Characterization

Since the methods available in the literature for lignin characterization are applicable primarily to lignins that are commercially available, such as from pulping processes (kraft or sulfite) and that can be used in polymeric applications, the methods of characterization developed have targeted these types of polymers. In contrast, biomass-to-ethanol pretreatment processes can produce very low-molecular-weight polymers. One major distinction between these types of processes is that conventional kraft pulping is usually performed under strong alkaline conditions. Most of the pretreatments employed to date are carried out under acidic conditions. There are commercial acidic processes such as the sulfite processes, but in this case, the lignins are modified by sulfonation, with the formation of the high molecular weight surfactants, the lignosulfonates. Methods of analyses for these commercial types of lignins differ substantially from those needed for the characterization of low molecular weight lignins.

Characterization studies started in FY 84 with a detailed investigation and characterization of steam exploded lignins. Mass balance data were obtained on the isolation of lignins from this pretreatment as a function of solvent (1985 Contractors report, Chum et al. 1985). The lignins were characterized as to the chemical functionalities present, molecular weight distribution, degree of carbon-carbon condensation, and spectroscopic techniques were employed to assess the structures of key components of these lignins (Chum et al. 1985, Chum et al. 1984). These studies led us, and other researchers worldwide, to realize that many methods proposed in the literature were not suitable for the analyses of lignins isolated from this pretreatment. These studies were carried out in very close contact with the French effort in steam explosion (e.g., Lachenal 1985, Bardet et al. 1985, Robert et al. 1987), the Canadian effort (Marchessault et al. 1982), and the Japanese work (e.g., Tanahashi et al. 1983). A collaboration with Dr. Danielle Robert from the Grenoble group started in 1985 in the area of NMR characterization of lignins.

The activities in FY 85 addressed the organosolv pretreatment carried out under controlled conditions, systematically varying the severity of the treatment; organosolv lignins were isolated in nearly quantitative yields, and comparative characterization studies between organosolv and steam exploded lignins begun (Chum et al. 1985). Three feedstocks were addressed in the organosolv pretreatment - aspen, black cottonwood, and bagasse. Comparisons between the lignins produced by these feedstocks and resulting lignin structures have been made in FY 86 and FY 87. In FY 87, in collaboration with the SERI Biotechnology Branch, studies of the lignins resulting from dilute acid hydrolysis of aspen followed by an alkaline delignification step have been carried out. The recent characterization work on organosolv and dilute hydrolysis aspen lignins is reported in this Proceedings.

In this period, SERI researchers with the collaboration of many scientists, addressed the development of new methods of analyses of the low molecular weight materials. Spectroscopic studies of organosolv lignins

were conducted with Professor J. Utley and Dr. C. Z. Smith from the Queen Mary College, University of London through a NATO grant (Hawkes et al. 1986). Improved synthetic methods for a few lignin model polymers were devised. A key question in lignin conversion is the weight of the polymers and their distribution. SERI researchers developed quantitative derivatization of lignins into soluble forms that allow quantitative molecular weight distribution studies (Chum et al. 1987) which have been adopted by many researchers in the field. Important studies were carried out, in collaboration with M. Himmel, on fast methods such as high performance size exclusion chromatography and the effects of solvents on the molecular weight distributions. Good progress has been made relative to the synthesis of lignin model polymers suitable for calibration of these molecular weight studies (Chum et al. in press).

Pretreatments that lead to low-molecular-weight aspen lignins are steam explosion and batch organosolv processes. These pretreatments substantially reduce the oxygen content of the lignins. For instance, the empirical formula of the resulting lignins under acidic conditions is $CH_{1.2}O_{0.35}$. Dilute acid hydrolysis process followed by alkaline delignification also produces relatively low-molecular-weight lignin structures. These three pretreatment methods produce suitable cellulosic feedstocks for enzyme hydrolysis. The dilute acid hydrolysis carried out in the plug flow reactor or in a percolating reactor produces higher molecular weight lignins that are substantially carbon-carbon bonded. Such materials are the hardest to fragment into suitable liquid fuels, except perhaps by fast pyrolytic processes (Diebold and Scahill 1987). The materials produced by pretreatments for enzyme hydrolysis are relatively small polymers, with 2-20 monomeric units linked together. Ether bonds between monomers still exist, although, depending on the pretreatment conditions, carbon-bonded structures start to become important. Substantial changes occur to the side chains of the lignins under these pretreatments; instead of three-carbon side chain structures, many of these pretreated materials have 2 or 1.5 as average side-chain size, which is composed of three, two, and one-carbon side chains per aromatic structure (see Chum et al. this Proceedings).

Some correlations between pretreatment and isolation conditions have been made and the degree of suitability of these lignins to further conversion is assessed. These studies also help design the appropriate conditions for successful pretreatments. Lignins from pretreatments for enzyme hydrolysis are the most suitable starting feedstocks for further conversion into monomeric aromatic compounds that are liquid fuels. The structure of the lignins is also a marked function of the starting feedstock. Hardwoods and grasses are the easiest materials to delignify (Sarkanen and Ludwig 1971).

Lignin Conversion Into Liquid Fuels Processes

The program efforts in lignin conversion to liquid fuels were initiated in March of 1985, with a thorough literature review of the conversion of lignins into low molecular weight compounds, performed with the collaboration of Dr. D. Goheen (E. Seidel and Associates) (Chum et al. in press and references therein). The review identified pyrolysis and mild hydrotreatment as the most attractive routes to convert lignins into low-molecular-weight phenolics or hydrocarbons, based on yields and available engineering data primarily on kraft lignins, lignosulfonates, and acid hydrolysis lignins.

Mild hydrotreating was selected as a promising alternative for the conversion of lignins into mixtures of low-molecular-weight phenolics and aromatic hydrocarbons for our initial experimental evaluation. In collaboration, research was begun with Professor Scott Cowley, Department of Chemistry, Colorado School of Mines (CSM), on the preparation of special catalysts with dual functionalities to allow the mild hydrodeoxygenation needed and also to build some dealkylation capability such that the lignin fragments produced are in the correct boiling range. In FY 86-87, special dual functional supported catalysts were identified for mild deoxygenation (based on metals such as molybdenum and molybdenum/nickel) and with acidic supports (aluminophosphates with various levels of phosphate to increase the acidity of the support and promote carbon chain cleavage). Mild routes were selected because excess hydrodeoxygenation and hydrogenation lead to excessive consumption of hydrogen and production of saturated hydrocarbons such as cycloparaffins, which are not as good octane enhancers as MAE or aromatic hydrocarbons.

In FY 86, a continuous trickle-bed reactor was set up at SERI such that the catalysts prepared and characterized at CSM could be tested by SERI researchers as to their ability to dealkylate and deoxygenate lignin model compounds. Initial results identified promising families of catalysts for such processes and that a substantial level of dealkylation can be obtained by increasing the acidity of the support to moderate levels (Ratcliff et al. 1987). The preparation, characterization, and testing of these catalysts with model compounds are described in this Proceedings (Ratcliff et al.)

In collaboration, research was also begun with Professor Robert Baldwin from the Department of Chemical Engineering of CSM in FY 86 in comparing the two prevalent methods of hydrotreating--batch and a simulation of continuous, batch with continuous product removal. Removal of volatile phenolic compounds was found to be essential to avoid char formation and increase phenolic yield (Ratcliff et al. in press). A 300 mL batch autoclave has been modified to allow continuous product removal. The operation and design of the autoclave are described in detail in this Proceedings (Johnson et al.).

FURTHER WORK

The catalyst development will provide novel catalytic systems to convert lignins into mixtures of phenolics and aromatic hydrocarbons. While in 1987 the work concentrated on systems that resemble those employed in petroleum and coal conversion, which require sulfidization to exhibit suitable performance, in 1988 new oxide systems will be investigated. A simpler, less expensive process operation is anticipated if this research is successful. In addition, a more rigorous economic evaluation of liquid fuels from lignins will be performed in collaboration with N. Hinman (Biotechnology Research Branch) in 1988. An engineering analysis of the lignin hydrotreating process will be conducted. The analysis will establish the relationship between key process parameters and economics. Process flow sheets will be prepared with mass/energy balances. Capital and operating costs will be determined and a spreadsheet developed. The economics of the hydrotreating process can then be integrated into the overall economics of biomass-to-ethanol.

If the research in 1987 and 1988 is successful, in FY 89 it is expected that the selection of catalysts for mild hydrodeoxygenation and dealkylation of lignins from biomass-to-ethanol processes will identify the best catalyst for investigations in a larger scale, to be conducted in an ebullated bed such as set up at Colorado School of Mines. These large-scale studies will continue through FY 91, such that data for a comprehensive economic evaluation can be obtained, thus improving the evaluation carried out in FY 88, with preliminary data.

In order to address the lignin conversion in a timely manner, it is imperative to know the key chemical structures present in the lignins from biomass-to-ethanol processes, and components derived from extractives and bark that will be present in the conversion process. This knowledge allows one to tailor the conversion process to the key components. Therefore, the program also addresses the chemical characterization of lignin polymers and additional components isolated after biomass pretreatment for ethanol production and the development of techniques for their chemical analyses.

In FY 89-91 the integration of feedstock-pretreatment-lignin conversion will be addressed. Key feedstocks identified by the Oak Ridge National Laboratory and submitted to pretreatment and lignin isolation are going to be investigated. They will be characterized and submitted to screening for conversion to liquid fuels. In parallel, method development will continue to achieve the most timely and cost-effective lignin analyses and potentially carbohydrate analyses methods for these feedstocks/pretreatment conditions.

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CATALYST DEVELOPMENT FOR HYDRODEOXYGENATION AND DEALKYLATION OF LIGNINS FOR FUELS

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ABSTRACT

The addition of phosphate, even in small amounts, has a significant effect on the properties of the support material of heterogeneous catalysts. The surface area passes through a maximum at a P/Al ratio of 0.1 before decreasing continuously with an increase in the P/Al ratio. The supports have unimodal pore distributions with the median pore size increasing with increasing P/Al ratio. An increase in the P/Al ratio results in material with a decreasing order of crystallinity, as evidenced by x-ray diffraction. The absence of alumina or aluminum phosphate crystals indicates that the supports are randomly arranged composite material rather than intimately mixed domains of alumina and aluminum phosphate.

The addition of phosphate to catalysts prepared by this method has a marked affect on the catalyst activity and selectivity. The catalyst screening with 4-propylguaiacol (4PG), a lignin model compound, has shown that the formation of phenolic compounds suitable for conversion to methyl aryl ethers for fuels is possible. A Ni-Mo catalyst having a phosphated alumina support (P:Al = 0.5) gave the highest yields of these compounds with hydrocarbons as the major side products. Initial tests with Mo catalysts suggest that the side product hydrocarbons can be biased in favor of aromatic hydrocarbons, which are more desirable as high-octane-fuel components and because they will consume less hydrogen in a lignin-to-liquid fuels process than the formation of cycloparaffins would. The Mo catalysts with phosphated alumina supports P:Al = 0.5 and 0.8 will be tested next to determine if higher selectivities to phenols, cresols, ethylphenols, etc., are possible while suppressing aromatic ring saturation as the results at P:Al = 0.2 suggest. The best catalysts will then be synthesized in larger quantities and tested with pretreated lignins in our parallel reactor engineering task.